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STUDY REPORTS:

MRID No. 45623408, Versol, P.L. & Abdel-Baky, S (2001) Magnitude of the Residue of BAS 510 UCF and BAS 500 F Residues in Mint and Mint Processed Fractions: BASF Study Number: 66700. Unpublished study prepared by BASF Corporation. 95 pages.

EXECUTIVE SUMMARY:

BASF Corporation has submitted field trial data for pyraclostrobin in/on mint. Five trials were conducted in regions: V: ID (1 trial) and MI (2 trials), XI: OR (1 trial) and WA (1 trial) during the 2001 growing season. The number and locations of field trials, including the four trials conducted in year 2001 (MRID 45623408), are in accordance with OPPTS Guideline 860.1500. The number and location of the field trials are sufficient to support a tolerance for mint.

At each test location, mint received four sequential foliar application of BAS 500 02F at a rate of 0.2 lb ai/A in combination with BAS 510 UCF, for a total seasonal rate of 0.8 lb ai/A. The retreatment intervals between the sequential applications were 7 (±1) days. Mint samples (leaves and stems) were harvested with preharvest intervals (PHIs) of 7 days and 14 or 15 days.

Also, at a field test site in Oregon, mint received four sequential foliar applications of BAS 500 02 F at a rate of 1.0 lb ai/A in combination with BAS 510 UCF, for a total seasonal rate of 4.0 lb ai/A (5x) for mint processing.

The method used to analyze the residues of pyraclostrobin and BF 500-3 in mint was LC/MS/MS BASF Method D9908. The method is adequate for data collection based on acceptable concurrent method recovery data. The limit of quantitation (LOQ) was 0.02 ppm for BAS 500 F and BF 500-3 in mint and mint oil.

The maximum storage interval of mint samples from harvest to analysis was 4 months. No mint storage stability data have been submitted. Available storage stability data indicated that residues of pyraclostrobin and its metabolite BF 500-3 are relatively stable under frozen storage conditions in/on fortified samples of grape juice, sugar beet tops and roots, tomatoes, and wheat grain and straw for up to 25 months, and in/on fortified samples of peanut nutmeat and processed oil for up to 19 months. The storage stability data can be translated to support the storage intervals for mint samples for this study (D269668, etc., L. Cheng, 11/28/2001).
The combined residues of pyraclostrobin (BAS 500 F) and its metabolite ranged from 2.51ppm

to 11.78 ppm with a PHI of 7 days and 1.82 ppm to 7.40 ppm with a PHI of 14 days reflecting the use of pyraclostrobin with the treatment of BAS 500 02 F on mint at the seasonal application rate of 0.8 lb ai/A.

STUDY/WAIVER ACCEPTABILITY/DEFICIENCIES/CLARIFICATIONS:

Under the conditions and parameters used in the study, the field trial residue data are classified as scientifically acceptable.

The acceptability of this study for regulatory purposes is addressed in the forthcoming U.S. EPA Residue Chemistry Summary Document DP Barcode D290342.

COMPLIANCE:

Signed and dated GLP, Quality Assurance and Data Confidentiality statements were provided. No deviations from regulatory requirements were reported.

A. BACKGROUND INFORMATION

Pyraclostrobin is a fungicide that is structurally related to the naturally occurring strobilurins, compounds derived from some fungal species. Pyraclostrobin is also in the same chemical class as azoxystrobin (PC 128810), registered for many crops and turf/lawn, and trifloxystrobin (PC 129112) which recently was granted a "reduced risk" status as a fungicide on many crops. The biochemical mode of action of these compounds is inhibition of electron transport in pathogenic fungi.

TABLE A.1. Test Compound Nomenclature

Compound	Chemical Structure

Common name	Pyraclostrobin
Company experimental name	BAS 500 F
IUPAC name	methyl N-{2-[1-(4-chlorophenyl)-1*H*-pyrazol-3-yloxymethyl]phenyl}(N-methoxy)carbamate
CAS name	methyl [2-[[[1-(4-chlorophenyl)-1*H*-pyrazol-3-yl]oxy]methyl]phenyl]methoxycarbamate
CAS #	175013-18-0
End-use product/EP	20% water dispersible granular formulation (WG; product name: Cabrio™ EG Fungicide; EPA Reg. No. 7969-187/EPA File Symbol 7969-RIT).

Pyraclostrobin technical is a white to light beige solid.

TABLE A.2. Physicochemical Properties

Parameter	Value	Reference[1]
Boiling point/boiling range	N/A	D290351
pH	N/A	D290351
Density	1.285g/cm^3 at 20°C	D290351
Water solubility (20°C)	2.41 mg/L in deionized water at 20°C 1.9 mg/L in buffer system pH 7 at 20°C 2.3 mg/L in buffer system pH 4 at 20°C 1.9 mg/L in buffer system pH 9 at 20°C	D290351
Solvent solubility (mg/L at 20°C)	acetone (≥160 mg/L); methanol (11 mg/L); 2-propanol (3.1 mg/L); ethyl acetate (≥160 mg/L); acetonitrile (≥76 mg/L); dichloromethane (≥110 mg/L); toluene (≥100 mg/L); n-heptane (0.36 mg/L); 1-octanol (2.4 mg/L); olive oil (2.9 mg/L); DMF (≥62 mg/L).	D290351
Vapour pressure at 25°C	2.6 x 10^{-10} hPa (at 20°C); 6.4 x 10^{-10} hPa	D290351
Dissociation constant (pK_a)	Does not dissociate in water. There are no dissociable moieties.	D290351
Octanol/water partition coefficient Log(K_{OW})	n-Octanol/water partition coefficient (K_{ow}) at room temperature (=K_{ow} of 3.80, pH 6.2; =log K_{ow} 4.18, pH 6.5).	D290351

B. EXPERIMENTAL DESIGN

B.1. Study Site Information

TABLE B.1.1 Trial Site Conditions

Trial Identification (City, State/Year)	Soil characteristics				Meteorological data	
	Type	%OM[1]	pH[1]	CEC[1] meq/g	Monthly rainfall average	Mean T (°F)
Grant, MI/2001	muck	NA[2]	NA	NA	NA	42-85
St. Johns, MI/2001	sandy loam	NA	NA	NA		54-83
Culver, OR/2001	sandy loam	NA	NA	NA		36-60
New Plymouth, ID/2001	silt sandy	NA	NA	NA		41-68
George, WA/2001	sandy loam	NA	NA	NA		30-62

[1] These parameters (percent organic matter, pH, and cation exchange capacity) are optional except in cases where their value affects the use pattern for the chemical.
[2] Not available.

TABLE B.1.2. Study Use Pattern.

Location (City, State/Year)	EP [1]	Application					Tank Mix Adjuvants
		Method/Timing	Vol, GPA[2]	Rate, (lb a.i./A)	RTI, [3] days	Total Rate, (lb a.i./A)	
Grant, MI/2001	BAS 500 2F (20%WG)	Foliar/4-8"	23-24	0.2	7±1	0.8	Latron B-1956
St. Johns, MI/2001	BAS 500 2F (20%WG)	Foliar/6-12" tall	23-24	0.2	7±1	0.8	Latron B-1956
Culver, OR/2001	BAS 500 2F (20%WG)	Foliar/pre-bloom 19" tall	20-21	0.2	7±1	0.8	Agri-Dex COC
New Plymouth, ID/2001	BAS 500 2F (20%WG)	Foliar/pre-bloom 20-26" tall	30	0.2	7±1	0.8	R-11 Spreader
George, WA/2001	BAS 500 2F (20%WG)	Foliar/16" tall	20	0.2	7±1	0.8	R-11 Spreader

[1] EP = End-use Product
[2] Gallons per acre, L/ha
[3] Retreatment Interval

TABLE B.1.3. Trial Numbers and Geographical Locations

Growing Region	Mint	
	Submitted	Requested
5	2	2

11	3	3
Total	5	5

B.2. Sample Handling and Preparation

After harvest, samples were placed in a freezer (< -10°C) upon arrival at BASF Agro Research. Mint samples were homogenized with dry ice before analysis.

The maximum storage interval of mint samples from harvest to analysis was 4 months. No mint storage stability data have been submitted. Available storage stability data indicated that residues of pyraclostrobin and its metabolite BF 500-3 are relatively stable under frozen storage conditions in/on fortified samples of grape juice, sugar beet tops and roots, tomatoes, and wheat grain and straw for up to 25 months, and in/on fortified samples of peanut nutmeat and processed oil for up to 19 months. The storage stability data can be translated to support the storage intervals for mint samples for this study (D269668, etc., L. Cheng, 11/28/2001) .

B.3. Analytical Methodology

The method used to analyze the residues of pyraclostrobin (BAS 500 F) and BF 500-3 in mint was LC/MS/MS BASF Method D9908. Homogenized mint samples are extracted with methanol:water:2N HCl (70:25:5, v:v:v) and filtered. An aliquot of the extract is removed and cleaned by liquid/liquid partitioning. Residues are further purified on a silica gel Speedisk micro column. Residues in mint oil are diluted with 10 mL of de-ionized water, purified by steam distillation for approximately 15 minutes. Residues are then partitioned into cyclohexane and further purified by silica gel column chromatography. The final residues are analyzed by LC/MS/MS. For quantitation, the product/daughter ion for the transition *m/z* 388 → 194 for pyraclostrobin (BAS 500 F) and *m/z* 358 → 164 for BAS 500-3 are measured. The limit of quantitation (LOQ) was 0.02 ppm for BAS 500 F and BF 500-3 in mint and mint oil.

Recovery values of pyraclostrobin from samples of mint leaves fortified over the concentration range of 0.02 to 40.0 ppm for leaves averaged 106 ± 14% for BAS 500 F and 113±19% for BF 500-3 (see Table C.1. for the recoveries of mint hay and oil).

C. RESULTS AND DISCUSSION

The analytical method (LC/MS/MS BASF Method D9908) is adequate as a data collection method. As shown in Table C.1, adequate method validation data for mint have been provided. The limit of quantitation (LOQ) was 0.02 ppm for BAS 500 F and BF 500-3 in mint.

As shown in Table C.2, the available information indicated that mint samples were stored for a maximum of about 4 months. As indicated in the previous studies, residues of pyraclostrobin and its metabolite BF 500-3 are relatively stable under frozen storage conditions in/on fortified samples of grape juice, sugar beet tops and roots, tomatoes, and wheat grain and straw for up to

25 months, and in/on fortified samples of peanut nutmeat and processed oil for up to 19 months. The storage stability data can be translated to support the storage intervals for mint samples for this study (D269668, etc., L. Cheng, 11/28/2001).

As indicated in Table C.3., five trials were conducted during the 2001 growing season. The number and locations of field trials, including the four trials conducted in year 2000 (MRIDs 45623408). The residues of pyraclostrobin and its metabolite BF 500-3 in/on all mint samples ranged from 2.51ppm to 11.78 ppm with a PHI of 7 days and 1.82 ppm to 7.40 ppm with a PHI of 14 days reflecting the use of pyraclostrobin with the treatment of BAS 500 02 F on mint at the seasonal application rate of 0.8 lb ai/A.

TABLE C.1. Summary of Concurrent Recoveries of Pyraclostrobin (BAS 500F) & its Metabolite (BF 500-3) from Mint

Matrix	Spike level (mg/kg)	Sample size (n)		Recoveries (%)		Mean ± std dev	
		BAS 500F	BF 500-3	BAS 500F	BF 500-3	BAS 500F	BF 500-3
tops	0.02-40.0	4	4	87, 105, 110,120	88, 115, 115,135	105.5± 13.82	113.25 ±19.29
Hay	0.02-100	2	2	70, 78	80, 85	74	82.5
oil	0.02-0.02	2	2	85,103	105, 106	94	105.5

TABLE C.2. Summary of Storage Conditions

Matrix (RAC)	Storage Temp. (°C)	Actual Storage Duration (months)	Interval of Demonstrated Storage Stability (months)
Analyte: Pyroclostrobin (BAS 500F) & its metabolite (BF 500-3)			
mint	≤-20±2	4	Residues of pyraclostrobin and its metabolite BF 500-3 are relatively stable under frozen storage conditions in/on fortified samples of grape juice, sugar beet tops and roots, tomatoes, and wheat grain and straw for up to 25 months, and in/on fortified samples of peanut nutmeat and processed oil for up to 19 months. The storage stability data can be translated to support the storage intervals for mint samples for this study (D269668, etc., L. Cheng, 11/28/2001).

TABLE C.3a. Residue Data from Mint Field Trials with Pryraclostrobin residues Treated with BAS 500 02 F at 1x the Proposed Use rate.

Trial ID (City, State/Year)	Region	Crop/Variety	Total Rate, (lb a.i./A)	PHI (days)	Residues (ppm)		
					BAS 500F	BF 500-3	Total
Grant, MI/2001	5	Peppermint/ Black Mitchum	0.8	7	9.45, 11.05	0.64, 0.73	10.09, 11.78
				14	6.85, 6.45	0.55, 0.55	7.40, 7.00
St. Johns, MI/2001	5	Spearmint/ Native	0.8	7	6.20, 6.10	0.19, 0.24	6.39, 6.34
				14	4.10, 4.65	0.15, 0.15	4.25, 4.80
Culver, OR/2001	11	Peppermint/ Native	0.8	7	3.05, 2.95	0.26, 0.35	3.31, 3.30
				14	1.80, 2.00	0.26, 0.28	2.06, 2.28
2.28New Plymouth, ID/2001	11	Peppermint/ Native	0.8	7	9.20, 8.20	0.77, 0.81	9.97, 9.00
				15	6.20, 6.55	0.64, 0.66	6.84, 7.21
George, WA/2001	11	Peppermint/ Native	0.8	7	2.35, 2.25	0.16, 0.20	2.51, 2.45
				14	1.80, 1.70	0.02, 0.20	1.82, 1.90

TABLE C.4. Summary of Residue Data from Crop Field Trials with Pyraclostrobin.

Commodity	Total Applic. Rate, (lb a.i./A)	PHI (days)	Residue Levels (ppm)						
			n	Min.	Max.	HAFT*	Median (STMdR[2])	Mean (STMR[3])	Std. Dev.
Analyte: Pyroclostrobin (BAS 500F) & its metabolite (BF 500-3)									
mint	0.8	7	10	2.51	11.78	10.94	6.37	6.51	3.53
	0.8	14	10	1.82	7.40	7.20	4.53	4.56	2.41

* HAFT = Highest Average Field Trial.
[2] STMdR = Supervised Trial Median Residue.
[3] STMR = Supervised Trial Mean Residue.

D. CONCLUSION

The combined residues of pyraclostrobin (BAS 500 F) and its metabolite ranged from 2.51ppm to 11.78 ppm with a PHI of 7 days and 1.82 ppm to 7.40 ppm with a PHI of 14 days reflecting the use of pyraclostrobin with the treatment of BAS 500 02 F on mint at the seasonal application rate of 0.8 lb ai/A.

E. REFERENCES

DP Barcodes: D269668, D272771, D272789, D274095, D274192, D274471, D274957, D275843, and D278429

Subject: PP#0F06139. PC Code 099100. Pyraclostrobin on Various Crops: Bananas (import), Barley, Berries, Bulb Vegetables, Citrus Fruits, Cucurbit Vegetables, Dried Shelled Pea & Bean (except Soybean), Fruiting Vegetables, Grapes, Grass, Peanut, Pistachio, Root Vegetables (except Sugar Beet), Rye, Snap Beans, Stone Fruits, Strawberry, Sugar Beet, Tree Nuts, Tuberous and Corm Vegetables, and Wheat. Review of Analytical Methods and Residue Data. EPA File Symbols: 7969-RIT, 7969-RIA. CAS #175013-18-0.
From: L. Cheng
To: C. Giles-Parker/J. Bazuin
Dated: 11/28/01
MRIDs: 45118428-451184-37, 45118501-45118512, 45118514-45118537, 45118601-45118625, 45160501, 45272801, 45274901, 45321101, 45367501, 45399401, and 45429901

F. DOCUMENT TRACKING

RDI: ChemTeam:06/29/04:L.Cheng:07/22/04
Petition Number:2F6431
DP Barcodes: D290342
PC Code:099100

Template Version September 2003